

Degradation Mechanisms of Materials for
Large Space Systems in Low Earth Orbit

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W. L. Gordon

R. W. Hoffman

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Department of Physics
Case Western Reserve University
Cleveland, Ohio 44106

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This study was initiated to explore degradation of various materials used in spacecraft after severe loss of polymeric material coatings (Kapton) was observed on an early shuttle flight in low earth orbit. Since atomic oxygen is the major component of the atmosphere at 300 km, and the shuttle's orbital velocity produced relative motion corresponding to $\sim 5\text{eV}$ of oxygen energy, it was natural to attribute much of this degradation to oxygen interaction. It was proposed to test this assumption employing facilities at NASA Lewis Research Center (NASA LeRC), such as large volume vacuum systems and ion beam sources, in an exploratory effort to produce atomic oxygen of the appropriate energy, and to observe mass loss from various samples as well as characteristic optical radiation. Simultaneously, it was planned to do ex-situ characterization of the surfaces of these samples by AES and energy dispersive SEM using facilities at Case Western Reserve University (CWRU).

Several investigations were initiated during the period of this grant and completed with the support of a subsequent grant and NASA LeRC in-house funds. The results of these investigations have been presented in four papers. Two of these papers have been published. Copies of the other two, which were prepared as internal communications, are appended to this report. As an aid to the reader, we summarize briefly the contents of each of these papers.

I. D. C. Ferguson, "The Space Shuttle Glow", unpublished. (Supported by Grant NAG 3-352).

This is a detailed analysis of the shuttle glow phenomenon. Possible mechanisms for the glow are described and critically discussed, including radiation from collisionally excited oxygen atoms and nitrogen molecules, dissociatively excited atomic oxygen, sputtering induced emission, and excited molecules due to recombination at the surface.

II. D. C. Ferguson, "Laboratory Degradation of Kapton in a Low Energy Oxygen Ion Beam", NASA Report No. TM-83530, 1983. (Supported by Grant NAG 3-352 and NASA LeRC in-house funds)

This paper describes the results of oxygen and argon ion bombardment of Kapton carried out in a large volume vacuum tank at NASA LeRC. Auger analysis of some of the samples bombarded in this facility was performed at CWRU.

III. D. C. Ferguson, "The Energy Dependence and Surface Morphology of Kapton Degradation Under Atomic Oxygen Bombardment", Proceedings of the 13th Space Simulation Conference (1984), pp. 205-221. (Supported by Grant NAG 3-352 and NASA LeRC in-house funds)

In this paper Dr. Ferguson used mass loss data for Kapton from a number of different investigations to fit an expression of the form

$R = \alpha E^n$, where R is the mass loss rate in atomic mass units per incident atom or ion, E is the impact energy in eV, and α and n are constants determined by the fit. He used plasma ash (0.1eV), atomic oxygen beam (1eV), shuttle (5eV), and his own ion beam (800eV) data to obtain $\alpha = 1.5$ and $n = 0.68$, with a correlation coefficient of 0.990 for his least-squares fit. Subsequent oxygen ion bombardment data, taken at CWRU in the energy range 43 to 188eV, agrees well with Ferguson's formula (Horton, et. al., J. Vac. Sci. Technol. A4, 1236 (1986)). This work at CWRU was supported by NASA Grant NAG 3-426.

IV. "Surface Analysis of STS 8 Samples", unpublished. (Supported by Grant NAG 3-352, Grant NAG 3-426, and NASA LeRC in-house funds)

This paper presents the results of Auger analysis of test samples flown on STS 8. The samples were prepared at CWRU and at NASA LeRC. The Auger analysis was performed at CWRU.

The Space Shuttle Glow

Dr. Dale C. Ferguson
Case Western Reserve Univ.

Abstract

The glow surrounding forward pointing surfaces of the Space Shuttle is examined. Possible mechanisms for the glow are described and critically discussed, including radiation from collisionally excited oxygen atoms and nitrogen molecules, dissociatively excited atomic oxygen, sputtering induced emission, and excited molecules due to recombination at the surface. It is hypothesized that emission from water vapor formed in excited states on the Shuttle surface may be the origin of the glow. The relation of the glow to the degradation of materials in the forward direction is discussed. Laboratory and space experiments are proposed to test the nature of the glow and to learn how to minimize its adverse effects.

INTRODUCTION

The Space Shuttle, operating in low earth orbit, surprisingly glows (1, 2). The orange-red glow, which is estimated (3) to be of an intensity of about 1 kiloRayleigh, occurs only above the surfaces of the Shuttle which are facing the direction of motion, and seems to be independent of the material of the exposed surfaces (4). The extent of the observed glow is a layer of perhaps 10 cm in depth surrounding the Shuttle surfaces, and a tail perhaps 3 meters in length extending back from the edge of the vertical stabilizer in the direction opposite that of vehicle motion (1). There are sharp shadows on vehicle parts shielded from the "ram" effect of the Shuttle motion, where no glow occurs. The glow is brightest when the line of sight skims a long section of exposed surface, implying that a long optical pathlength helps build the intensity of the glow. The spectrum obtained by a diffraction grating flown on STS-4 has not yet been fully analyzed. The glow seems to have been weaker (5) on STS-4 than on STS-3.

The glow is of concern for many reasons. Obviously it will interfere with experiments (astronomy, etc.) which require or measure low light levels. Furthermore, it indicates that there are processes occurring in low earth orbit which are poorly understood and unanticipated. If the glow is related to oxidation processes or other processes which may cause degradation of materials, it may be extremely important to understand its nature. The performance and lifetime of large solar arrays and other "permanent" orbiters may depend on that understanding. In this report,

we consider the processes which may contribute to the glow, in an attempt to discover what is causing it and how it may be circumvented or prevented from adversely affecting performance and test conditions in low earth orbit.

ELEMENTARY DEDUCTIONS

The glow is obviously not confined to the surface and its extent is not an effect of overillumination of the photographic film or videocameras; this may be clearly seen in the excellent photo published in Aviation Week, where the "tail" of emission extending away from the vertical stabilizer is seen to be reflected in its tiles, with the dark shadow of the stabilizer wake in between. Thus, the emission is truly extended in space, and must be due to emitters coming off the Shuttle surfaces.

An estimate of the lifetime of the emitting species may be made from the extent of the emission layer in the ram and wake directions. At the altitudes where the Shuttle was operating (280 to 305 km), the mean free path of atoms or molecules (5,6) is of the order of 2000 meters, so that we can assume the emitters radiate without colliding with the surrounding medium (see footnote). The extent of the glow in the direction opposite that of vehicle motion may be taken to be given by the Shuttle velocity times the emitter lifetimes. The Shuttle orbital velocity of 7.9 km/s then yields an emitter lifetime of about 4×10^{-4} second.

Another estimate of the emitter lifetime may be obtained by assuming that the emitters are coming off the ram-side surfaces with essentially thermal velocities. At a temperature of about 300K, a species with an atomic weight of 30 amu will have a total velocity given by

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \quad , \text{ so that}$$

$$v = \sqrt{\frac{3kT}{m}} \quad ,$$

and taking the velocity perpendicular to the surface to be 1/3 the total velocity, we find that

$$v_{\perp} = \sqrt{\frac{kT}{3m}} \quad , \text{ or } v_{\perp} = 1.7 \times 10^4 \text{ cm/s.}$$

Dividing the glow depth in the ram direction by this velocity, we find a lifetime of about 6×10^{-4} sec. For atomic oxygen ($m = 16$ amu) the lifetime becomes about 4×10^{-4} sec. For atomic argon ($m = 40$ amu) the lifetime is about 7×10^{-4} sec. Thus, we have consistent estimates for the emitter lifetime of about 4 to 7×10^{-4} sec.

Since the glow only occurs in the ram direction, we can assume that

Footnote. If the pressure increases to about 10^{-3} torr near the Shuttle during thruster firing, collisions may, however, be important.

the energy is supplied by the impinging species impacting on the surface at orbital velocity. Table 1 gives the energies of the major impacting species, along with their abundances at an altitude of 280 km and their dissociation and ionization energies (6,7). It can be seen from this table that O and N₂ are the species most likely to be energetically responsible for the excitation of energy levels of less than about 9 eV, although O₂ and A may be important for energy transfers of 10 and 13 eV per collision if these become implicated. Notice also that O₂ impacts with sufficient energy to dissociate, while N₂ does not. Thus, atomic oxygen may be more readily available for chemical reactions at surfaces than atomic nitrogen.

Taking the wavelength of the orange-red glow to be about 7000 Å, we find that the excitation energy required for the responsible transitions is about 2 eV, so that H and He may be excluded from the list of exciting species, if we restrict the excitations to single events.

Finally, taking the intensity to be 1 kiloRayleigh, and remembering (8) that 1 Rayleigh = 10^6 photons/cm² sec emitted in all directions from a vertical column, we find that for each cm² of surface we have about 2×10^9 eV/sec in glow emission. This is only a small fraction of the energy impinging on the surface for any of the major impacting species. Thus, no information is contained in the glow intensity about the exciting species.

The impact of the atomic and molecular species does not appreciably heat the surface. If all of the major species gave up their entire energy on impact, the total heat transfer would be about 4.6×10^{15} eV/cm² sec. This compares to a radiative flux out of a black body at 300K of about 3×10^{17} eV/cm² sec. Thus, a change of perhaps 1% in the energy flux could be produced. This would raise the temperature of the surface by less than 1K.

POSSIBLE MECHANISMS

We can come up with several possible mechanisms for the glow. They include the following;

1. Direct collisional excitation of the backscattered species.
2. Dissociation of molecular oxygen at the surface into excited atoms.
3. Sputtering of excited atoms from the impacted surfaces.
4. Molecular recombination of atoms at the surface into excited states.

There are advantages and disadvantages of each of these explanations for the Shuttle glow. In the next section we will examine each of these possibilities in turn and will attempt to come to a conclusion as to which is most probable. Finally, we will discuss experiments which can help clarify which mechanism is responsible and what can be done to minimize or eliminate the adverse effects of the glow.

DISCUSSION OF OPTIONS

- A. Direct excitation of backscattered species.

To see if this is possible, we need to compare the timescales

involved in the collisions with those in the emitted radiation. We will assume that electronic states can be excited if the wave frequencies of the transition are comparable to the frequencies involved in the collisions. An estimate of the time needed for a collision (for reacceleration in the opposite direction) can be made by dividing the collisional radius by the atomic velocity. In our case, we can find the collisional radius from the collision cross-section σ for neutral atoms and molecules (9),

$$\sigma = \pi r_c^2 \approx 10^{-15} \text{ cm}^2$$

which gives

$$r_c \approx 1.8 \times 10^{-8} \text{ cm} \approx 1.8 \text{ \AA}$$

Then, the collision time t_c is

$$t_c = \frac{r_c}{v} = \frac{1.8 \times 10^{-8}}{7.9 \times 10^5} \approx 2 \times 10^{-14} \text{ s.}$$

A time t_e associated with the electronic transition is the inverse of the frequency ν ,

$$t_e = \frac{1}{\nu} = \frac{\lambda}{c}$$

where λ is the wavelength and c is the speed of light, which for $\lambda \approx 7000 \text{ \AA}$ gives

$$t_e \approx 2 \times 10^{-15} \text{ s.}$$

Thus, the collision time is about ten times longer than the time related to the transition. We should expect only a small fraction of the backscattered atoms to have electrons in the excited state. This is no great limitation on the mechanism, for if only one oxygen atom in 6×10^5 is backscattered in the excited state the observed photon intensity could be produced. The ratio for argon would be one atom in 30. Any or all of the major species (excluding H and He) could be excited enough to produce the glow.

We now ask which backscattered species have a spectrum which can produce the orange-red glow. Spectra obtained by S. Mende (3) on STS-4 seem to show diffuse emission from about 6300 \AA to 8000 \AA , the limit imposed by the optics used. Assuming no species can be excited to an electron energy higher than its impact energy, we obtain (10,11,12) the possible atomic energy levels listed in Table 2. Since the collisions take place with a surface matrix, we need not worry about selection rules for excitation. Possible emission bands for incident molecules (13,14) are given in Table 3. From these tables it can be seen that atomic argon has no emission lines in the orange-red part of the spectrum and may be dropped from further consideration. Atomic oxygen has two forbidden lines in the orange, and both N_2 and O_2 have emission bands in about the right wavelength range. The $B^3\Pi_g - A^3\Sigma_u^+$ (1st positive) bands of N_2 show their strongest intensity in the afterglow at about 5800 \AA (yellow-orange) but the $b^1\Sigma_g^+ - X^1\Sigma_g^+$ (atmospheric) bands of O_2 show up strongest in emission between 7600 and 8000 \AA (deep red-infrared). Thus, the best candidates for the emission, if it is due to collisional excitation of the impacting species, would seem to be the forbidden lines of atomic oxygen and the

atmospheric bands of molecular oxygen. The radiative lifetime of the atmospheric bands of O_2 (25) is about 12 seconds. It is intriguing to note that the atomic lines of oxygen and the molecular bands of O_2 both come from metastable states, with lifetimes much greater than that of the emitting species, about 5×10^{-4} second. However, these are purely radiative lifetimes. If collisional de-excitation is important, the effective lifetime of metastable states can be considerably reduced.

It is worthwhile to ask at this stage whether radiation from backscattered species has been observed in the laboratory. The answer is yes. Emission by backscattered atoms is routinely observed in sputtering experiments where surfaces are bombarded with high energy ions. Although these experiments have been done with much higher incident energies than those on the Space Shuttle, we feel that they can be informative. Kerkdijk and Thomas (18) report that bombardment of gold and nickel surfaces by H^+ and He^+ ions of > 2 keV led to excited emission of H and He above the surfaces. The velocities of the reflected excited beams were nearly the same as those of the incident beams, implying that little energy transfer occurred aside from the electron capture and excitation. One expects that in the process of collision with the surface the incident ions capture electrons with little energetic effect well before scattering occurs. Kleckner and Clark (19), colliding beams of atomic hydrogen with gaseous A, N_2 , O_2 and CO_2 , obtained cross-sections for excitation of the 4s state of hydrogen at 5 keV of about $2 \times 10^{-18} \text{ cm}^2$. This result implies that the excitation by neutral collisions is not insignificant even for collisions with free particles. One expects inelastic scattering to be orders of magnitude more likely with a surface matrix. Whether the kinetic energy of the incoming atoms and molecules is transferred to the matrix or results in electron excitation of the backscattered species is another question.

Studies of the interaction of low energy atomic and molecular beams with surfaces have paid little attention to the emission from the backscattered beam. They have established conclusively, however, that inelastic collisions are commonplace. Defining, after Kogan (20), the energy accommodation coefficient α_E by

$$\alpha_E = \frac{E_i - E_r}{E_i - E_w}$$

where E_i is the incident beam energy, E_r is the reflected beam energy, and E_w is the energy of the reflected beam if it were in thermal equilibrium with the surface, we see that perfectly elastic collisions will result in an accommodation coefficient of 0 while perfectly inelastic collisions will result in a value of 1. Measured values (21) of the accommodation coefficients for atomic and molecular beams of energies of a few eV typically are larger than $\frac{1}{2}$. A study of the sticking probability of potassium atoms impinging on a tungsten surface at eV energies (22) showed that at energies less than about 8 eV more than 20 % of the incident atoms lost so much energy that they were trapped by the surface. This shows that at the low energies in Space Shuttle conditions inelastic collisions with the surface are common. These lead to thermalization of the reflected atoms at the surface and justify our use of the surface temperature in calculating velocities of reflected species for determination of radiative lifetimes. They also make plausible the hypothesized transfer of kinetic energy into electronic excitation of the backscattered atoms and molecules. Unfortunately,

experiments measuring the amount of this excitation at low energies have not been done.

B. Dissociation of O_2 at the surface into excited O atoms.

Energetically, it is quite possible for an O_2 molecule, striking a surface, to dissociate into excited O atoms. With 10.4 eV of impact energy, and 5.2 eV needed to dissociate, one could then have 5.2 eV of electronic excitation left over. The excitation could be evenly distributed between the two atoms or one atom could be more highly excited than the other. However, we can be sure that dissociation will produce a large supply of excited O atoms, since the dissociation is a process which pulls the electrons into higher orbits. The number of excited O atoms produced by this process will be roughly 2% of the ^{number} of atoms of incident oxygen, so that whether the O is mainly excited by dissociation or by direct collisional excitation will depend on the unknown fraction of impinging O atoms which are excited. In both processes excess energy will be radiated away by the surface in a continuum with a cutoff at 5.2 eV.

In the dissociation process, however, it is possible for one of the atoms to escape from the surface with an excitation greater than 5.2 eV. This is because one of the atoms could be left bound to the surface, while the atom which leaves could take up the energy deficit in the form of electronic excitation. Thus, if the radiation is due to molecular oxygen dissociated into atoms at the surface, we could expect to see lines from states as high as 5.2 eV plus the binding energy of O to the surface. If the binding energy is greater than about 3.9 eV, then, the allowed transitions of O at 1356 Å and 1359 Å would be possible, with lifetimes (23) of 8×10^{-4} s and 3×10^{-3} s. If the glow were not orange-red, one would suspect these transitions to be its origin, because their lifetimes are so similar to that observed. At any rate, the presence or absence of these lines in the glow may determine whether dissociation of molecular oxygen is an important contributor.

C. Sputtering of excited atoms from the impacted surfaces.

It is observed when sputtering atoms from the surfaces of semiconductors, metals, and metallic oxides that excited atoms are often seen to radiate just above the surface. The emission intensities are increased, and the velocity of the major emitters is decreased, when there is a thin layer of metal oxide on the metal surface or when oxygen is admitted to the experimental chamber (27). In order for this process to occur, surface atoms must actually be sputtered from the surface. It is a reasonable question to ask whether the energies of the species impinging on the Shuttle surface are high enough to cause sputtering to occur.

Sputtering threshold energies for various materials have been measured most noticeably by Morgulis and Tishchenko (28) and by Stuart and Wehner (29). Unfortunately, their results do not agree. The thresholds obtained by Stuart and Wehner are between 2 and 3 times those obtained by Morgulis and Tishchenko for identical sputtering and sputtered species, and give threshold energies uniformly above 11 eV, while those of Morgulis and Tishchenko are uniformly below 13 eV! Much of the discrepancy may be due to the peculiar shape of the yield curve near zero yield as seen by

Morgulis and Tishchenko (30). The results of Stuart and Wehner are extrapolated from higher energies and must miss this kink in the curve. This effect seems to occur for yields less than about 10^{-3} atoms per sputtering ion, so that for the energies of atoms impinging on the Shuttle, we can take that to be an upper limit to the yields in our case.

Tolk et al (31) found that for all the surfaces they tested, the optical line emission from sputtered species went to nearly zero at impingement energies lower than about 40 eV, but they made no measurements at ion energies less than 30 eV. Their derived excitation efficiency curve is still increasing at energies less than about 150 eV, although they think it must turn down for energies much below that. Without any hard evidence that it does, we must make the conservative assumption that it does not, and work to find a maximum possible value for the emission.

According to Tolk et al (31), the excitation function may be taken to be a constant (which they have assigned a value of 1) for ion energies greater than about 1 keV, and the excitation function at about 150 eV then has a value of about 6.5. Tsong and Yusuf (32) give absolute photon yields for sputtered atoms using 20 keV A^+ ions. Let the sputter yields (atoms/ion) be called Y . Let the absolute photon yields at 20 keV (photons/atom sputtered) be called p . Then let the normalized excitation function at low energies (photons at 150 eV/ photons at 20 keV) be called e . Then, the number of photons L produced per cm^{-2} per second by the spacecraft surface moving at speed v through a medium of number density N becomes

$$L = N v Y p e .$$

Taking $N = 8 \times 10^8 \text{ cm}^{-3}$, $v = 8 \times 10^5 \text{ cm/sec}$, $Y = 10^{-3}$, $p = 10^{-2}$ (about the maximum yield found by Tsong and Yusuf (32)) and $e = 6.5$, we find

$$L = 4 \times 10^{10} \text{ photons/cm}^2 \text{ sec} .$$

This compares very favorably with the observed intensity of about 10^9 photons per cm^{-2} sec for the glow, with a comfortable margin for overestimates in any of the yields. Thus, light emission from sputtered atoms is a viable mechanism to produce the glow intensity. Ca has an allowed transition at 6572 Å which has a long lifetime. The silicon forbidden lines at 6527 and 6590 Å are attractive because the Shuttle tiles are largely SiO_2 , and other surfaces are likely to be contaminated by Si sputtered from the tiles.

One interesting feature of the radiation from sputtered atoms in explaining the Shuttle glow is that the excitation of the atomic levels of the sputter emitters is approximately that expected for thermal equilibrium at a high temperature (33,34). Surface analysis by spectrophotometry of excited states from bombardment uses the thermodynamic approximation for line strengths, but there appears to be some controversy over whether line strengths really follow the LTE rule (35), so the question remains open.

It goes without saying that more work needs to be done on sputtering induced atomic line radiation. The sputtering thresholds of Stuart and Wehner (29) even depend on atomic line radiation which they assumed to be excited by the surrounding plasma. It is not clear to what extent they were measuring, instead, sputter induced radiation. The work of Tolk et al

(31) should be repeated at lower ion energies, and it should be established, once and for all, whether the Boltzmann distribution of excited states holds for this type of excitation.

It should be mentioned that molecular band and continuum emission have also been seen to occur above sputtered surfaces (27). Hydrocarbon contamination leads to bands of CH, nitrogen implanted silicon shows bands of N₂ upon bombardment, and a continuum is seen above bombarded iron, nickel, titanium, and other metals. Oxidation seems to enhance the continuum level, as does the presence of CO contamination (36). Clearly, more work needs to be done on sputter induced emission at low energies.

D. Chemical combination of O with O or other elements to produce excited molecules

The oxygen impinging on the Shuttle surfaces may stick and combine chemically with surface atoms or with other oxygen atoms to produce free molecules in excited states. The most obvious possibility is that molecular oxygen will be formed, which may then leave the surface and radiate. The "wall" recombination rate for oxygen atoms has been determined (24) to be about 5×10^{-7} . That is, for every oxygen atom hitting the wall, there will be a probability of 5×10^{-7} that it will combine with another oxygen atom. It is not known how this probability changes with material, temperature, or pressure.

Using this recombination rate, we can calculate the possible rate of emission from excited O₂ molecules. Since 6.2×10^{17} O atoms impinge on each cm² of surface per second, there will be 3.1×10^{11} O₂ molecules/cm² sec formed by wall reactions. An intensity of 1 kR is 10^9 photons/cm² sec. Thus, if only 1 molecule in 300 were formed in an excited state, the observed intensity would be produced.

Of course atomic oxygen will combine with many other elements on the surfaces, the activation energy being provided by the impacts. The relative surface independence of the glow makes combination with surface contaminants more attractive than combination with the surface materials themselves. Such chemical action can not only lead to drastic changes in the sputtering rate, but can also lead to the production of volatile molecules, free to radiate from their excess combination energy. Among the oxides which have molecular bands in the orange-red are those listed (26) in Table 4.

We investigated the report (15) that the glow becomes brighter after the reaction control system thrusters fire by reviewing a videotape kindly provided us by Roger Williamson. It showed that a firing of the forward control thrusters produced no visible effect on the glow above rear surfaces, but firing the rear thrusters produced a brightening of the glow for a period of a few seconds. We now inquire as to the exhaust products which could lead to surface contamination. The primary exhaust products from the thrusters are (16) N₂, H₂O, H₂, CO₂ and CO, in the order of molecular abundance. Perhaps the most attractive of these as a surface contaminant is H₂O. Oxygen impacting on the surface could combine chemically with it to produce excited H₂O. The strong emission bands of H₂O start at about 6400 Å and extend through the red into the infrared. Furthermore, we estimate that in a minimal vernier thruster firing (39), about 3×10^{10} molecules of H₂O are produced. If 1% of these molecules returned to the Shuttle and all of them stuck to its surfaces, the

coverage would exceed 8×10^{11} molecules/cm². Then, assuming a wall combination rate of 5×10^{-4} , it would take about 3 seconds for the H₂ produced to be exhausted by combination of the H₂ with incoming O atoms. Furthermore, during that time, we calculate that if every combination produces a photon from an excited H₂O, there will be about 3×10^{11} photons/cm² sec produced. For comparison, the impact rate of atomic O on the surface is 8.8×10^{10} atoms/cm sec. If all of the impacting hydrogen atoms stuck and produced H₂ molecules, which were subsequently combined with impacting oxygen atoms to make excited water vapor, the photon production rate would be about 4.4×10^{10} photons/cm² sec. Of course in neither case will all of the atoms and molecules stick and/or be excited. However, assuming that only 1 in 40 molecules sticks and is excited upon combination, we can account for the intensity of the glow, its spectrum, and a sixfold increase in intensity for a few seconds after the thrusters fire.

Still, the most likely surface contaminant is atomic oxygen, and the incoming oxygen atoms should combine with it to produce excited molecular oxygen. The oxygen bands already discussed would then be produced also. We consider it most likely that both molecular oxygen and water vapor are being produced in excited states by combination at the surface with impacting oxygen atoms. As we shall see in the next section, there is real doubt as to whether the metastable states of molecular oxygen contribute much to the narrow glow layer, however.

THE LIFETIME PROBLEM

The lifetimes of most allowed transitions ($\sim 10^{-8}$ s) is much shorter than the calculated lifetimes of the glow emitter ($\sim 5 \times 10^{-4}$ s). Radiative lifetimes of forbidden transitions are usually much longer than this (~ 1 to 1000 sec). Thus, the lifetime of the glow emitters is a problem. How can one modify the radiative lifetimes to fit the observations?

One way to increase the apparent radiative lifetimes of allowed transitions is to have an intensity near that needed for saturation. That is, if the number of absorptions roughly equals the number of emissions per unit length, the apparent lifetime may become quite long. We may derive conditions necessary for this to occur. Let \tilde{K}_ν be the atomic or molecular absorption coefficient at frequency ν , I_ν be the specific intensity, s be the pathlength, and \mathcal{E}_ν be the emission coefficient (37). Then, radiative transfer implies that

$$\frac{dI_\nu}{ds} = -\tilde{K}_\nu I_\nu + \mathcal{E}_\nu$$

In terms of the Einstein coefficients,

$$\tilde{K}_\nu = \frac{N_1}{4\pi} B_{12} h\nu$$

$$\mathcal{E}_\nu = \frac{N_2}{4\pi} [A_{21} + B_{21} I_\nu] h\nu$$

$$B_{21}/B_{12} = g_1/g_2$$

$$\text{and } B_{21} = A_{21} \left(\frac{c_2}{2h\nu^3} \right)$$

where g_1 and g_2 are the statistical weights of the energy levels and h

is Planck's constant. Rewriting the equation of transfer, we have

$$4\pi \frac{dI_\nu}{ds} = N_2 A_{21} h\nu \left[1 - \frac{c^2}{2h\nu^3} \frac{N_1}{N_2} \left(\frac{g_2}{g_1} - \frac{N_2}{N_1} \right) I_\nu \right]$$

The apparent lifetime of an emitter is proportional to

$$\left(\frac{dI_\nu}{ds} \right)^{-1},$$

which for an isolated emitter is

$$(N_2 A_{21} h\nu)^{-1}.$$

When the emission must pass through absorbers, however, the specific intensity becomes important, and the apparent emitter lifetime goes up by the factor

$$\left[1 - \frac{c^2}{2h\nu^3} \frac{N_1}{N_2} \left(\frac{g_2}{g_1} - \frac{N_2}{N_1} \right) I_\nu \right]^{-1}$$

If we want this factor to be large, as it must be if we are to increase the apparent lifetimes of our allowed transitions to the observed glow emitter lifetime, we must have

$$\frac{c^2}{2h\nu^3} \frac{N_1}{N_2} \left(\frac{g_2}{g_1} - \frac{N_2}{N_1} \right) I_\nu \simeq 1.$$

For $N_2 \ll N_1$, as is usually the case, we have

$$I_\nu \simeq \frac{N_2 g_1}{N_1 g_2} \frac{c^2}{2h\nu^3}.$$

Let us assume that N_2/N_1 is given by the Boltzmann equation for a gas at a temperature T and use the observed specific intensity to see what excitation temperature is required for saturation. We then have

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{(E_2 - E_1)}{kT}}$$

where E_2 and E_1 are the energy levels involved. For a total intensity of 1 kiloRayleigh = 10^9 photons/cm² sec into 4π steradians, and a bandwidth $\Delta\nu$ of 1000 Å, we obtain at 7000 Å

$$I_\nu \simeq \frac{10^9 h\nu}{4\pi \Delta\nu} \simeq 4 \times 10^{-18}$$

and $\frac{2h\nu^3}{c^2} \simeq 1.2 \times 10^{-3}$, so that

$$\frac{N_2 g_1}{N_1 g_2} \simeq 5 \times 10^{-21},$$

and our assumption that $N_2 \ll N_1$ is upheld. From Boltzmann's equation above, we then have

$$\frac{E_2 - E_1}{kT} \simeq 46.8$$

and with $E_2 - E_1 = 1.78$ eV, we have $T \simeq 440$ K. This is not an unreasonable excitation temperature, since we expect surface temperatures near 300K and electron temperatures near 1000K. Thus, the lengthening of apparent lifetimes

of allowed transitions through near saturation seems to be a viable mechanism.

However, there appears to be another possibility for changed apparent radiative lifetimes. Metastable states may be collisionally de-excited before they radiate, so that only those which have radiatively decayed before a non-radiative transition will be seen. Thus, the apparent lifetime (and total intensity) of forbidden transitions may be lessened in the ratio of the time between collisions to the radiative lifetime. For ambient pressures in 300 km orbit the mean free path of atoms is much greater than the thickness of the Shuttle glow layer. However, it has been reported (40) that after thruster firings the pressure near the Shuttle can rise to about 10^{-4} torr. This can decrease the mean free path significantly, and thereby decrease the apparent width of a forbidden line layer. The mean free path λ_o is given by

$$\lambda_o = (\sigma N)^{-1}$$

where σ is the collision cross-section and N is the number density. Taking $\sigma \approx 10^{-15} \text{ cm}^2$ for collisional de-excitation and N to be given by the ideal gas law with $T \approx 300\text{K}$ (equivalent to the assumption of complete thermalization above the surfaces),

$$\lambda_o \approx 41.4/P \quad (P \text{ in dyne/cm}^2), \text{ or}$$

$$\lambda_o \approx 3.1 \times 10^{-2}/P \quad (P \text{ in torr}).$$

In order to have a layer 10 cm thick around the Shuttle, we thus need a pressure of about 3×10^{-3} torr. We must emphasize that this result is highly dependent on the cross-section assumed. A cross-section 10 times larger, which sometimes applies in cases of collisional line broadening, brings this result more nearly into agreement with the maximum reported pressures. However, if this mechanism applies, the depth of the glow layer should change with changes in the ambient pressure; i.e. with thruster firings. Viewing of the videotapes supplied us by Roger Williamson convinced us that no such narrowing of the glow layer follows thruster firings. Thus, all forbidden line and band explanations of the glow appear to be in conflict with the observations.

RELATION TO DEGRADATION

The Space Shuttle glow is related to another phenomenon observed on the STS-3 flight; the degradation of materials in the ram direction (38). Both only occur on forward facing surfaces, both may make use of the energy of the impacting species, and both may require the presence of atomic oxygen. In the case of the material degradation, it is believed that oxidation of plastics, paints, and graphite lead to volatile gases which escape, leaving a damaged surface. In the case of the Shuttle glow, oxidation of surface contaminants may lead to free molecules in excited states, the extra energy being supplied by the oxygen impact. One might suspect that both are manifestations of the same phenomenon. The relative amounts of chemistry involved in the two processes ^{may} differ, however.

MOST PROBABLE CAUSE OF THE GLOW

Clearly, the simplest explanation of the Shuttle glow would be the excitation of atomic oxygen atoms as they impact on the surface, followed by radiation of forbidden lines as they leave the surface. Arguing against this simple interpretation is the fact that the emission seems to be more diffuse than in the form of spectral lines, and that the lifetimes of the forbidden transitions involved are too long to produce the narrow glow layer. The same objections apply to the forbidden lines of sputtered atoms and to atomic lines of dissociated O_2 . The so-called pre-dissociation radiation from molecules about to dissociate ~~may~~ escape both objections. Radiation in the orange-red from bound O_2 molecules, however, shares the objection of having too long a radiative lifetime, and must be discarded.

Perhaps the most attractive explanation for the glow is from excited H_2O molecules leaving the surface. They are ordinarily formed by combination of H atoms on the surface to form H_2 , followed by combination with impacting O atoms to produce excited H_2O . When the nearby thrusters fire, more H_2 arrives at the surfaces, increasing the combination rate and the intensity of the glow momentarily. The nature of the surface is unimportant so long as the hydrogen sticks to it. The spectrum naturally extends from about 6500 Å through the red into the infrared region. Excited O and O_2 are also produced at the surface, but because their relevant transitions are forbidden, the emission extends over too wide a spatial range to be visible. The intensity of the H_2O radiation is limited by saturation of the emission by absorption, increasing thereby the apparent radiative lifetime by large factors. Collisional de-excitation is relatively unimportant due to the tenuous nature of the ambient gas even when the thrusters are firing.

If our hypothesis is true, then infrared spectra of the glow should show strong emission bands characteristic of H_2O vapor. High resolution spectra should show individual lines in the emission bands with widths corresponding to temperatures of 400-500K. Water dumps from the Shuttle should not increase the glow intensity except by photo-dissociation of water in sunlight, when the glow is too faint to be seen above the background anyway. It could be possible to increase the intensity of the glow by pumping the escaping unexcited H_2O up to higher energy levels artificially. Controlled leaks of hydrogen or other gases onto surfaces could be tried to see if the glow intensity or depth would change. Laboratory experiments with oxygen beams on hydrogen prepared surfaces could be done. A multitude of experiments spring to mind.

It is intriguing to think that the Space Shuttle glows because it is slowly burning off the hydrogen on its surface, a celestial flame, orange-red, lighting its own way through the night.

FURTHER WORK NEEDED

First of all a good, high resolution spectrum of the Shuttle glow is essential. The spectrum must have sufficient spatial resolution to distinguish the surface itself from the glowing layer above and sufficient spectral resolution to accurately identify the wavelengths of the bandheads and to find individual lines. The spectrum should extend into the infrared. The spectrograph should have a high quantum yield to adequately measure the faint Shuttle glow.

Secondly, the effects of altitude on the glow should be determined.

Mechanisms which are rate limited by the impacting flux of oxygen should depend on the oxygen number density directly. Those involving the presence of H_2 should depend on its density, etc. The glow should stop entirely at altitudes where the kinetic energy per incoming atom is insufficient to excite the radiating species. Controlled dumps of different gases could pick out those important for the chemistry. Surfaces could be heated to drive off impurities to check the influence on the glow intensity, and to find the effect of temperature on the reaction rates. Surfaces with a variable angle of attack could be used to determine the incident particle energies necessary. Finally, incoming particles could be ionized and surfaces charged to varying potentials to determine the exciting particle energy threshold.

Reaction rates for chemical combination of atomic oxygen with surface adsorbents should be determined in the laboratory at low pressures. Sticking probabilities and accommodation coefficients, as well as excitation probabilities, should be determined for the major impacting species at eV energies. Wall recombination rates should be determined for hydrogen, and the pressure dependence of the rate for oxygen found. Realistic sputtering thresholds need to be determined independent of the emission from sputtered species, and sputter induced emission should be thoroughly studied at energies near threshold.

Finally, the Space Shuttle conditions should be simulated as closely as possible in the laboratory. Neutral beams of atomic oxygen, molecular nitrogen, etc., should be fired at various materials in high vacuum to investigate the phenomenon thoroughly. Both contaminated and clean surfaces should be tested. Energy dependences should be examined. In short, all possibly important factors should be varied under controlled conditions to determine the source and nature of the glow, its relationship to material degradation, and steps which can be taken to minimize or eliminate its adverse effects.

ACKNOWLEDGMENTS

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Table 1

Species	Number density (cm ⁻³)	Impact Energy (eV)	Ionization (eV)	Dissociation (eV)
O	7.8x10 ⁸	5.2	13.6	
N ₂	1.8x10 ⁸	9.1	15.6	9.9
He	8.3x10 ⁶	1.3	24.5	
O ₂	8.1x10 ⁶	10.4	12.1	5.2
H	1.1x10 ⁵	0.3	13.6	
A	3.9x10 ⁴	13.0	15.8	

Table 2

Species	Impact Energy (eV)	Excitable E Levels (eV)	Wavelengths (Å)	Rad. Lifetimes (s)
O	5.2	0.02 1.96 4.17	5577 6300 6364 2958 2972	0.75 200 610 2700 15
A	13.03	11.56 11.63 11.73 11.84 12.91	9123 9658 10470 1067 1048	4.7x10 ⁻⁸ 1.7x10 ⁻⁷ 8.5x10 ⁻⁹ 8.4x10 ⁻⁹ 2.0x10 ⁻⁹

Table 3

Molecule	Impact Energy (eV)	Excitable Emission Bands	Wavelength Range (Å)
----------	--------------------	--------------------------	----------------------

N ₂	9.1	$a^1\Pi_g - X^1\Sigma_g^+$	< 2000-2600
		$a'^1\Sigma_u^- - X^1\Sigma_g^+$	
		$B'^3\Sigma_u^- - X^1\Sigma_g^+$	
		$A^3\Sigma_u^- - X^1\Sigma_g^+$	2300-5100
		$B^3\Pi_g - A^3\Sigma_u^+$	5000-10500
		$B'^3\Sigma_u^- - B^3\Pi_g$	6700-8700
		$B'^3\Sigma_u^- - X^1\Sigma_g^+$	2000-2200
O ₂	10.4	$B^3\Sigma_u^- - X^3\Sigma_g^-$	1800-4400
		$b^1\Sigma_g^+ - X^3\Sigma_u^-$	5400-8800
		$A^3\Sigma_u^+ - X^3\Sigma_u^+$	2600-4900
		$a'\Delta_g - X^3\Sigma_g^-$	10700-12700
		$A^3\Sigma_u^+ - b^1\Sigma_g^+$	3700-4800

Table 4

Oxides having molecular bands between 6300 Å and 8000 Å

MgO	SbO
NiO	TiO
ZrO	NO ₃
SmO	BiO
CO	LaO
O ₂	WO
CuO	CeO
CrO ₇	CaO
O ₂	OH
ScO	NO
H ₂ O	VO
BaO	BeO
CbO	

Surface Analysis of STS 8 Samples

Introduction

In order to provide information about the oxygen interaction with materials in low earth orbit, a number of test samples were prepared and flown on STS 8. We report the results on 7 flight samples and their corresponding backup samples, which were maintained in a laboratory environment for the same period of time. For the most part, both the flight and the backup samples were highly contaminated with surface carbon, probably as a result of their storage. Normally, only small differences were noted in the AES spectra between the flight and backup samples, but the chromium and copper specimens were notable exceptions.

Sample Documentation

The samples that were flown came from several sources and are described in Table I. The metal-backed thin Kapton, Teflon, and Mylar samples were representative of the polymers used for thermal blankets, many of which are known to degrade rapidly in LEO. Other specimens were prepared as films deposited on sapphire or quartz substrates. The ITO and MgF_2 are used as conducting or AR coatings for solar cells while the chromium, aluminum, and copper samples are representative metals chosen for their possible inertness to the oxygen beam. Of the samples listed in Table I, seven were selected for the Auger analysis and the data are reported here.

AES Analysis

All of the AES analyses were taken with a Physical Electronics double-pass CMA. For the metallic samples, in which there were no charging or decomposition difficulties, beam currents of a few μA were used with electron beam energies of 2 keV. For the polymer samples the beam current was decreased to

approximately 20 nA and for those samples for which charging was observed the primary electron beam energy was decreased to near the second SEE cross-over to minimize charging effects. The electron beam spot size on the specimen was approximately 0.5 mm diameter, minimizing the current density and thus the degradation of the insulating materials under the beam exposure. We have used such techniques earlier in the examination of samples for their SEE.

In contrast to our earlier work, the Teflon did not give rise to the maximum charging difficulties. However, the Kapton and Mylar flight samples, especially after sputtering, experienced such charging that the data quality was affected. All samples were examined in UHV before sputtering. Not unexpectedly, large amounts of carbon and oxygen were found as the result of the specimen handling or storage. The samples were then re-examined after sputtering with argon at a pressure of approximately 6×10^{-5} Torr. AES spectra were observed after approximately one minute sputter intervals until the surface carbon contamination was removed and data representative of the sample appeared. Normally this took place in about two minutes of sputtering with a total sputter current of about 2.5 μ A at 2 keV Ar^+ ions. Calibration in this system indicates a sputtering rate of 6 \AA per minute on SiO_2 .

The spectra were examined and the line identifications made. Atomic compositions were determined for representative samples using the published sensitivity factor technique with corrections where needed for beam energy changes. The relative accuracy of the AES technique must be taken as a few percent.

Results

Typical Auger spectra are shown for the copper flight sample in Fig. 1 and the copper backup sample in Fig. 2, in both cases before (a) and after (b) sputtering. In addition to the expected carbon, oxygen, and copper peaks, contamination by chlorine was also observed. Table II and III show the surface atomic

compositions for the polymer and thin film specimens respectively in before- and after-sputtering conditions. We discuss each briefly.

The Kapton shows a decided carbon enrichment compared to the expected stoichiometry. This has been noted earlier by the NASA-Ames group as well as in our own laboratory.

The Teflon samples appear to show fluorine desorption after sputtering. This, again, is not unexpected, and there appears to be little difference between the flight and backup specimens.

The Mylar flight sample after sputtering was the most difficult from the charging point of view and larger uncertainties must be associated with its composition values. The charging difficulties make the Auger peaks much broader and hence affect any analysis based on peak to peak values.

The chromium on Kapton substrate beam currents were restricted to 20 nA, even though direct charging was not observed. The separation of chromium from oxygen is difficult because of peak position interference, although the LMM-529 eV line has been used to identify chromium in Cr_2O_3 enriched stainless steel. The flight sample was about 1/3 oxygen with the remaining surface carbon being replaced by nickel after sputtering for three minutes. No peak representative of metallic chromium was found in the flight sample, but the negative going oxygen peak was smaller and broader than it would be for elemental oxygen. The presence of major nickel contamination was unexpected but confirmed by the backup sample in which both chromium and nickel peaks were present. It should be noted that while the backup sample contained some oxygen after four minutes of sputtering, presumably because of the difficulty of preparing oxygen free chromium films, the oxygen level was reduced by a factor of three in the backup sample compared to the flight sample. On the basis of the surface analyses we must conclude that the sample was changed substantially by exposure in LEO.

The ITO sample was distinguished by the absence of tin and the presence of a surface contamination of chromium in the backup sample. After sputtering there appears to be little difference between the flight and backup specimens.

The Molybdenum sample, after sputtering, also showed little difference between the flight and backup specimen. However, the sample was by no means metallic molybdenum. It appeared to be a mixed oxy-nitride with approximate composition of $M(ON)_3$.

The copper specimen showed a substantial difference between the flight and backup samples. Ignoring the contamination with chlorine, after the same sputtering time we find carbon in the backup sample and large amounts of oxygen in the flight sample. Assuming the initial compositions to be the same, this could be interpreted as a removal of carbon from the copper sample by interaction with the oxygen and desorption as CO or CO_2 plus a copper oxide formation during LEO exposure.

To summarize in an oversimplified way, the metallic chromium and copper samples showed substantial surface interactions during exposure on STS 8. On the other hand, the surface analyses of the polymer samples showed little difference between the flight and backup samples.

Table I
STS 8 Samples

Sample #	Description
1*	5 mil Kapton on Al
2*	5 mil Teflon on Inconel-Silver
3*	5 mil Mylar on Al
4	MgF ₂ on glass
5*	ITO on glass
6	SiO ₂ + PTFE on Kapton
7	Al ₂ O ₃ on Kapton
8	SiO ₂ on Kapton
9	TiO ₂ on quartz
10*	Molybdenum on sapphire
11*	Copper on sapphire
12*	Chromium on Kapton on Al
13	Optical reflector

*AES at Case Western Reserve University

Table II

Atomic %

		CARBON	OXYGEN	FLUORINE	CHROMIUM	NICKEL	Sputter (min)
KAPTON	FLT	bs 94.5	5.5	/	/	/	0.0
		as 91.1	8.9	/	/	/	2.0
	BCKP	bs 94.5	5.5	/	/	/	0.0
		as 89.9	10.1	/	/	/	2.0
TEFLON	FLT	bs 35.8	0.0	64.2	/	/	0.0
		as 49.6	0.0	50.4	/	/	2.0
	BCKP	bs 36.9	0.0	63.1	/	/	0.0
		as 47.9	0.0	52.1	/	/	2.0
MYLAR	FLT	bs 95.2	4.8	/	/	/	0.0
		as 90.0	10.0	/	/	/	1.0
	BCKP	bs 93.7	6.3	/	/	/	0.0
		as 93.8	6.2	/	/	/	3.0
Cr:KAPTON	FLT	bs 66.0	34.0	/	0.0	0.0	0.0
		as 0.0	34.2	/	0.0	65.8	3.0
	BCKP	bs 75.8	24.2	/	0.0	0.0	0.0
		as 4.3	12.2	/	13.8	69.8	4.0

BEAM CURRENT (I) = 20 nA
b

Table III
Atomic %

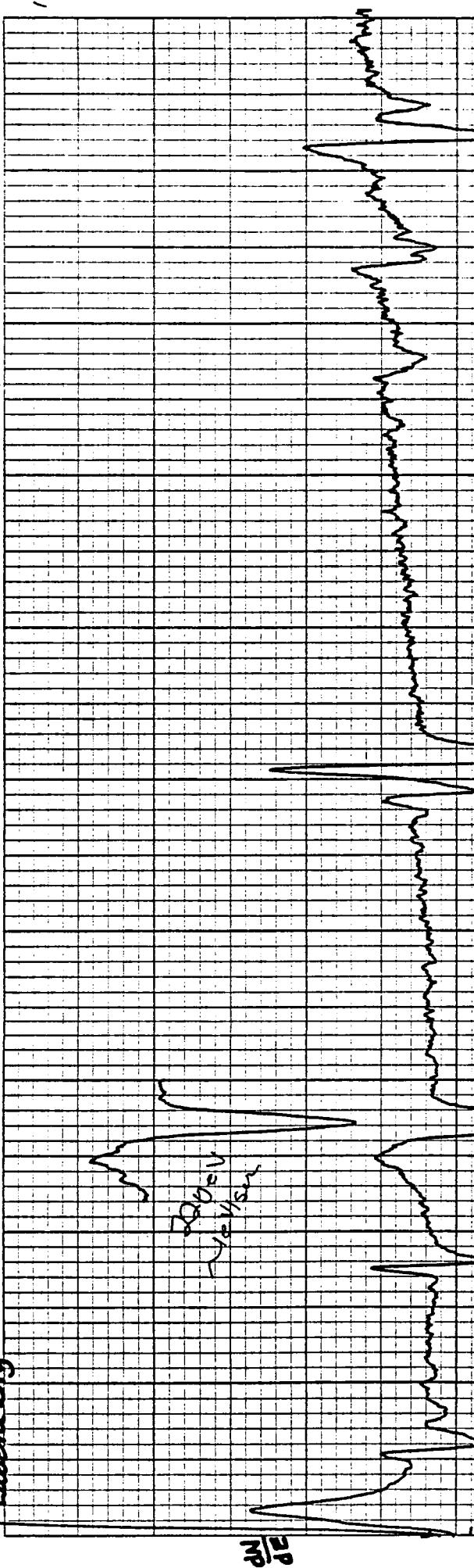
		C	O	Mo	Cu	In	Sn	Cr	C1	N	Sputter (min)
ITO	FLT	bs	29.7	44.9	/	/	25.3	0.0	0.0	/	0.0
	as	0.0	59.4	/	/	40.6	0.0	0.0	/	/	1.0
BCKP	bs	54.9	29.9	/	/	10.8	0.0	3.6	0.8	/	0.0
	as	4.4	57.6	/	/	36.2	0.0	1.5	0.2	/	4.0
FLT	bs	19.7	51.6	13.5	/	/	/	/	/	15.2	0.0
	as	0.0	62.0	26.2	/	/	/	/	/	11.8	2.0
MOLY	bs	26.6	48.4	12.1	/	/	/	/	/	12.9	0.0
	as	3.0	59.4	23.5	/	/	/	/	/	14.0	2.0
COPPER	bs	39.7	18.5	/	36.8	/	/	/	5.0	/	0.0
	as	0.0	28.6	/	67.7	/	/	/	3.7	/	3.0
BCKP	bs	64.5	4.4	/	28.3	/	/	/	2.8	/	0.0
	as	8.1	2.4	/	89.5	/	/	/	0.0	/	8.0

ITO, I = 2.0 μ A; MOLY and COPPER, I = 6.0 μ A
^b

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Laboratory

AUGER ELECTRON SPECTRUM

Sample: Cu #11 fit
(1a)



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Figure 1(a)

1000
600
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ELECTRON ENERGY (eV)

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Surface Physics
Laboratory

AUGER ELECTRON SPECTRUM

Sample: Cu #11 flat

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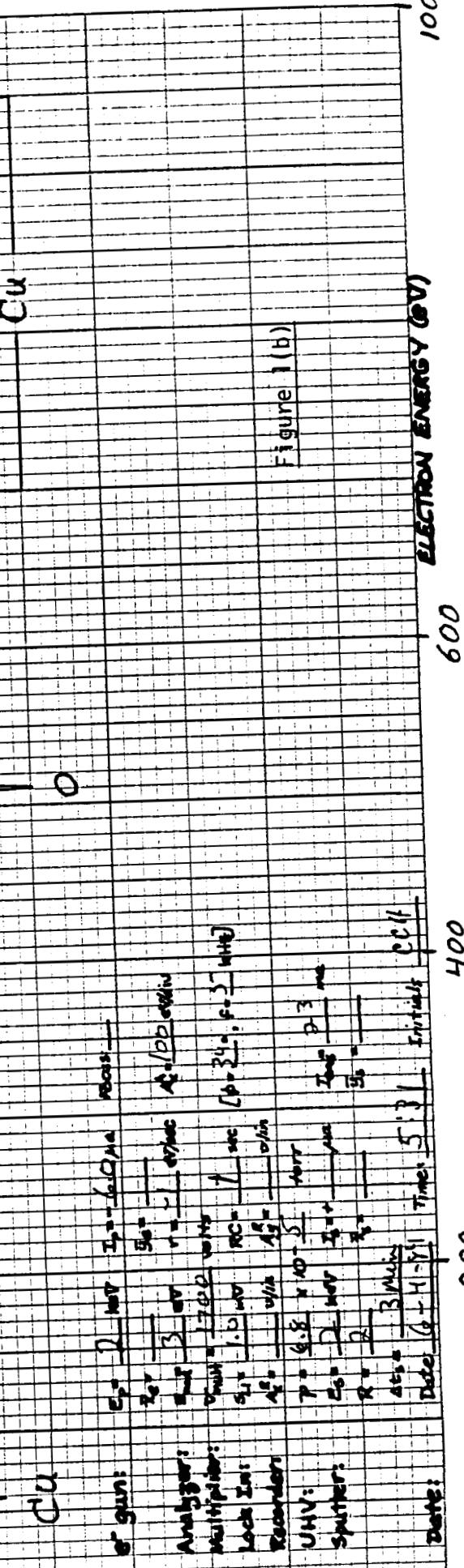


Figure 1 (b)

ELECTRON ENERGY (eV)

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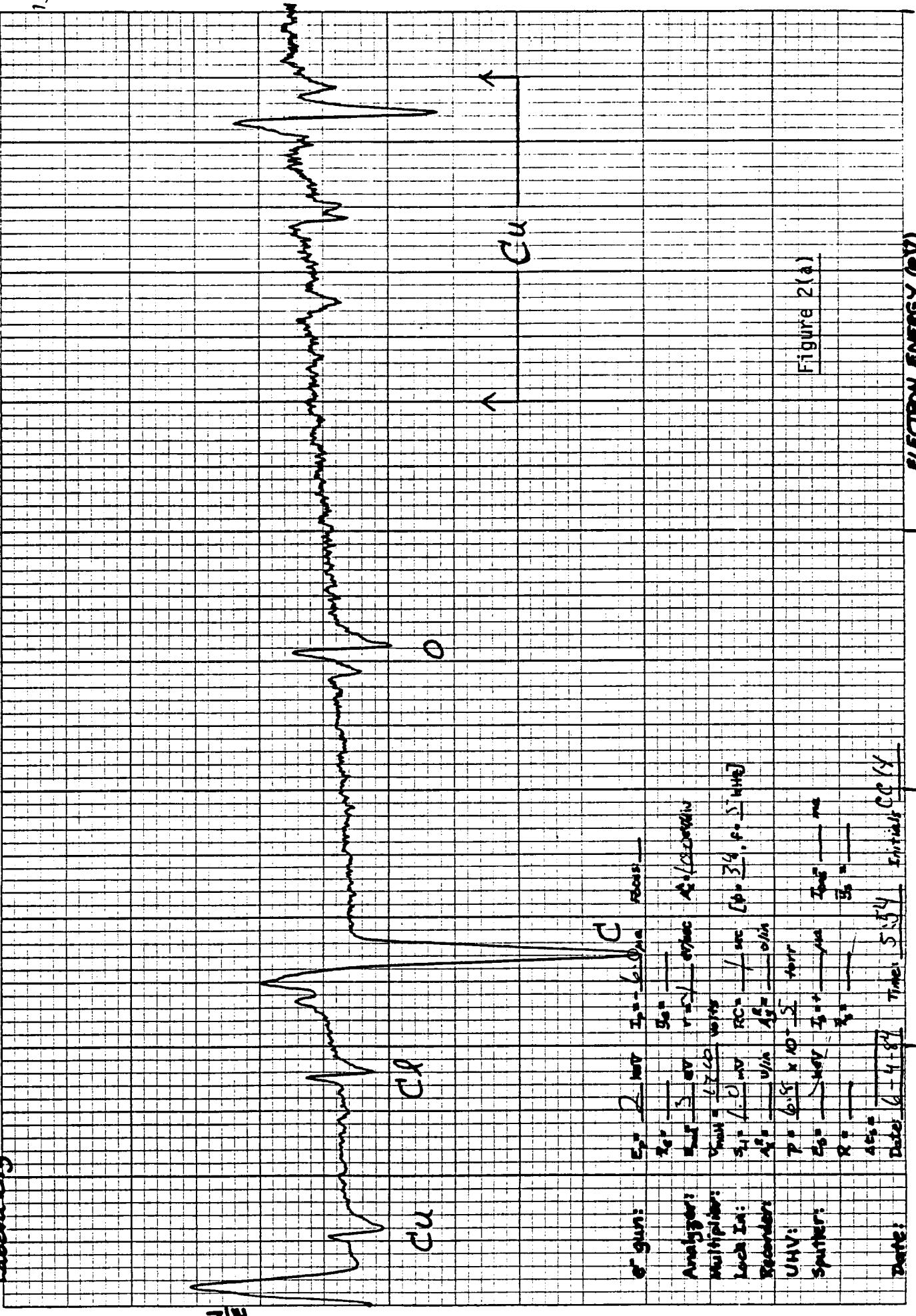
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AUGER ELECTRON SPECTRUM

Sample: Cu #11 Backscattered

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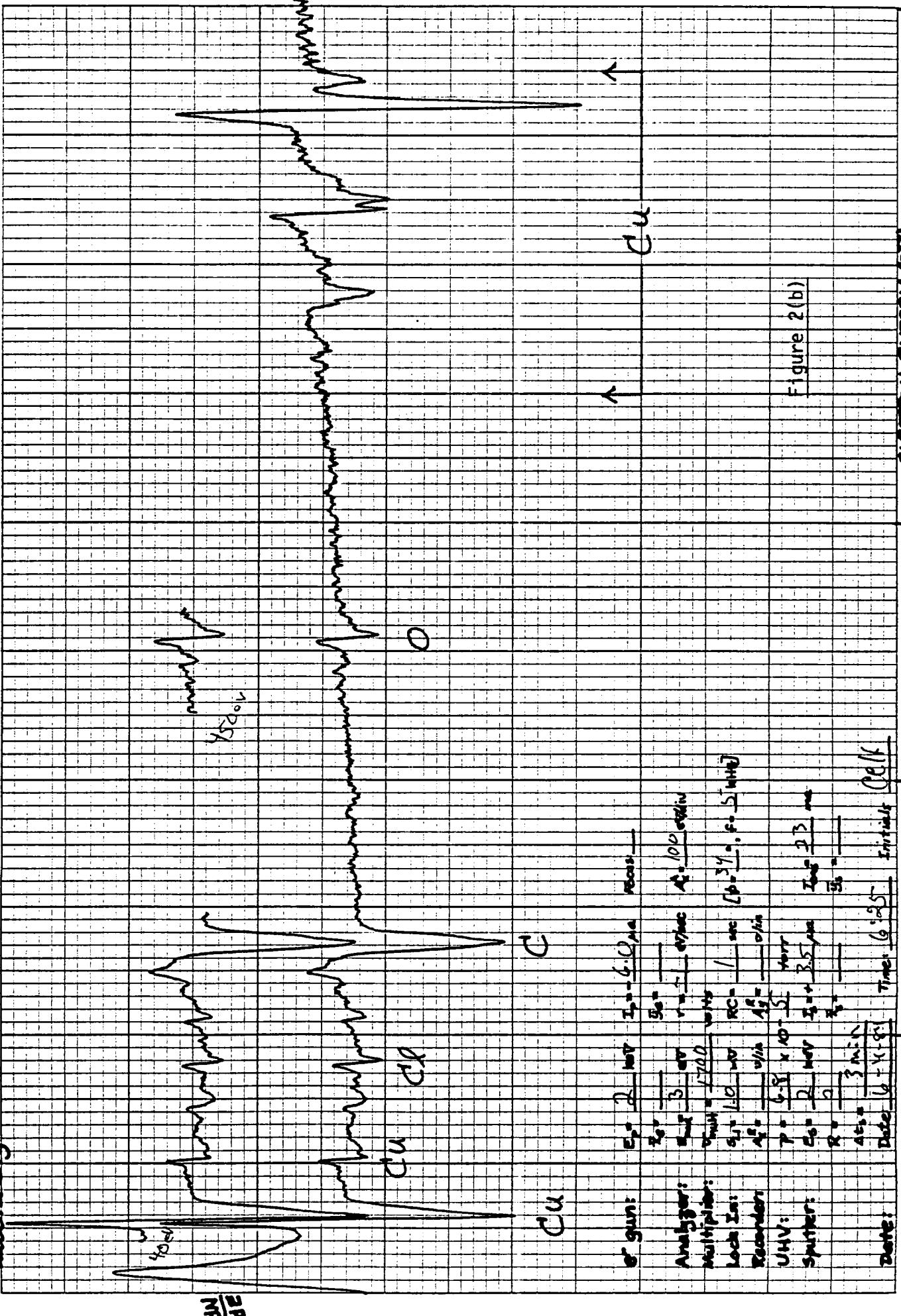
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AUGER ELECTRON SPECTRUM

Sample: Cu #11 Backup

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